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㊹発明の名称　熱収縮性ポリウレタンフイルム

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明　細　書

1．発明の名称

熱収縮ポリウレタンフィルム

2．特許請求の範囲

結晶融解熱 0.1乃至3.0cal/gの熱可塑性ポリウレタン樹脂よりなるフィルムであって、該フィルムの 120℃グリセリン浴中での熱収縮率が長さ及び幅方向の少くともいずれか一方に20%以上であり、且つ永久伸びが30%以下であることを特徴とする熱収縮性ポリウレタンフィルム。

3．発明の詳細な説明

［産業上の利用分野］

本発明は、各種物品の収縮用包材として極めて好適な、突刺、衝撃等の機械的強度に優れた熱収縮性ポリウレタンフィルムに関する。

［従来の技術］

従来より、収縮包装用フィルムとしては、ポリ塩化ビニル系、ポリプロピレン系、ポリエチレン系などの熱収縮性フィルムが知られ、それぞれの特徴を活した分野で広く利用されている。

しかしながら、これらのうちポリ塩化ビニル系熱収縮フィルムは、低温収縮性に優れるが、反面熱シールの際に塩素ガスが発生したり、あるいは可塑剤等の移行による衛生上の問題に加えて、引張、引裂、突刺、衝撃等の機械的強度に乏しいといった数多くの欠点を有している。また一方、ポリプロピレン系及びポリエチレン系熱収縮フィルムはコストが安く汎用されているが、収縮温度が比較的高い上にこの場合も突刺、衝撃等の強度が弱く裂けやすいという問題を有するなど、これら既存の収縮包装用フィルムは、そのいずれをとってみても突刺、衝撃等に対する抵抗性の点でユーザーの要望に応えられるものが見当たらないのが現状である。

［発明が解決しようとする課題］

本発明は、かかる事情に鑑みなされたものであり、その目的とするところは、柔軟で、引張、引裂等の強度が強く、しかも突刺、衝撃等の外力に対してとりわけ優れた抵抗性を有する熱収縮性ポリウレタンフィルムを提供する点にある。

［課題を解決するための手段］

本発明者等は、前記目的を達成するために、機械的強度が強く、しかも柔軟性と弾力性に関して優れた性質を有する熱可塑性ポリウレタン樹脂に着目し、該ポリウレタン樹脂ベースの熱収縮性フィルムについて鋭意検討した結果、特定の結晶性と熱収縮性並びに永久伸びを有するポリウレタンフィルムであれば、これまでのポリ塩化ビニル系樹脂等の熱収縮フィルムには見られなかった優れた突刺、衝撃等の機械的強度を有する、収縮用包材として好適なフィルムが得られることを見い出し、本発明を完成させた。

即ち、本発明は結晶融解熱 0.1乃至3.0cal/gの熱可塑性ポリウレタン樹脂よりなるフィルムであって、該フィルムの 120℃グリセリン浴中での熱収縮率が長さ及び幅方向の少くともいずれか一方に２０％以上であり、且つ永久伸びが３０％以下であることを特徴とする熱収縮性ポリウレタンフィルムに係るものである。

以下、本発明の熱収縮性ポリウレタンフィルムについて詳しく説明する。

本発明において熱可塑性ポリウレタン樹脂とは、二官能性ポリオールとジイソシアネート及びグリコールを主原料としてなる分子構造中にウレタン基を含有するゴム状弾性高分子のうち、熱可塑性を有するものを総称し、具体的には使用される前記ポリオール等の原料の種類によって区別されるところのアジペートエステル系、ポリエーテル系、カプロラクトンエステル系、ポリ炭酸エステル系等の熱可塑性ポリウレタン樹脂の一種又は二種以上からなるものであって、且つその結晶融解熱が 0.1乃至3.0cal/g、好ましくは 0.5乃至2.0cal/gのものである。

ここで、熱可塑性ポリウレタン樹脂の結晶融解熱が0.1cal/g未満の場合は、粘着性が強く、内包する物品とフィルムとが密着しやすいために、密着した部分が収縮不足となったり、あるいはひきつり現象を生じて外観不良を呈するなど、収縮用包材として致命的な問題が発生するのに対し、結晶融解熱が3.0cal/gより大きくなると、柔軟性、弾力性、更には熱収縮性等が低下して、本発明の目的とするような熱収縮性フィルムが得られない。

尚、本発明で使用する熱可塑性ポリウレタン樹脂は、結晶融解熱が前記条件を満足するものであれば、結晶性を有する熱可塑性ポリウレタン樹脂と結晶性を持たない通常の熱可塑性ポリウレタン樹脂をブレンドして用いることができるほか、その性質を大きく変えない範囲内でポリ塩化ビニル系、ポリエステル系、ポリアミド系、アクリル系、ポリオレフィン系等の熱可塑性樹脂をブレンドしたり、あるいは耐候性、取扱い性等を向上させる目的で紫外線吸収剤、酸化防止剤、着色剤、滑剤等を必要に応じて適宜添加してもさしつかえない。

本発明の熱収縮性ポリウレタンフィルムはまた、該フィルムの 120℃グリセリン浴中での熱収縮率が長さ及び幅方向の少なくともいずれか一方に２０％以上、好ましくは３０％以上であって、且つ永久伸びが３０％以下、好ましくは２０％以下でなければならない。

なぜなら、本発明者等は、柔軟性と弾力性に特異な性質を有する熱可塑性ポリウレタンフィルムを収縮用包材として用いた場合、比較的低い収縮率でも優れた緊縛性が得られる点に着目し、該フィルムの収縮率と包装後の緊縛性並びに突刺、衝撃などに対する抵抗性について詳しく検討した結果、フィルムの収縮率が大きくなると緊縛性は向上するが、反面分子配向が進みすぎて永久伸びが増大し、突刺、衝撃等の機械的強度が低下するという現象がみられるなど、熱収縮率と永久伸びの両者が特定の条件を満足してはじめてポリウレタンフィルムの収縮用包材への応用が可能になるからである。

従って、本発明のポリウレタンフィルムにおいて、 120℃グリセリン浴中での熱収縮率が長さ及び幅方向の少くともいずれか一方に２０％未満の場合は、収縮不足となって包装後の仕上り外観が悪くなる一方、フィルムの永久伸びが３０％より大きくなると突刺、衝撃等の機械的強度が大幅に

低下して、ポリウレタンフィルムの特性が失われるという不都合な問題が生じる。

尚、本発明において、ポリウレタンフィルムの熱収縮率をグリセリン浴中での値として表した理由は、収縮包装の際に通常よく用いられる熱風あるいはスチーム等の熱媒に比べて、フィルムへの熱伝導が均一で、熱収縮率を正しく定量評価できるためである。

また、本発明の熱収縮性ポリウレタンフィルムの厚さは、その用途に応じて適宜選択されるもので特に限定する必要はないが、フィルム強度、緊縛性、経済性、更には内包される物品へのフィット感等を考慮した場合、フィルム厚さは、通常10乃至300μのものが好適である。

［実施例］

以下、本発明の熱収縮性ポリウレタンフィルムについて、実施例により更に詳しく説明する。

尚、本発明において行った物性の測定法及び評価方法は次の如くである。

(1) 結晶融解熱

差動走査熱量計（DSC）に15mgの試料を入れ、これを15℃/minの昇温速度で昇温し、融解時にあらわれる発熱ピークの面積から発熱量を求め、これを試料1g当りに換算して求めた。

(2) 熱収縮率

試料フィルムを120℃グリセリン浴中に10秒間浸漬し、その間の熱収縮率を求めた。

(3) 永久伸び

ダンベル1号形に打抜いた試料フィルムを、標線間の伸びが100%に相当する長さに引張り、10分間保持したのち収縮させ、次式により永久伸びを測定した。

$$\text{永久伸び}(\%) = \frac{L_1 - L_0}{L_0} \times 100$$

L_0：標線間距離

L_1：収縮させた後の標線間距離

(4) 突刺強度

直径75φの円筒状リングの断面に、試料フィルムを張せて固定した後、該円形フィルム面の中心に先端角53度の円錐ヘッドを100mm/minの速度で突刺し、フィルムに穴が開くまでの最大荷重（単位：g）を突刺強度とした。

(5) 衝撃強度

振子式衝撃試験機（東洋精機製作所製フィルムインパクトテスター）を用い、フルスケール30kg-cm、衝撃ヘッド1/2インチの条件で衝撃強度（単位：kg-cm）を測定した。

(6) 収縮包装後の外観

トンネル内温度約140乃至150℃、通過時間約10秒に設定した収縮トンネル装置を用いて、試料フィルムが二軸収縮性の場合（実施例1～7、比較例1～4）は三方シール包装によって、また試料フィルムが一軸収縮性の場合（実施例8～10、比較例5～6）はスリーブシール包装によってそれぞれスプレー容器を収縮包装した。包装後の状態を目視で評価し、緊縛性、外観共に良好なものを（○）、緊縛性が悪いかあるいは著しい収縮むらが認められたものを（×）とした。

(7) 総合評価

突刺強度、衝撃強度及び収縮包装後の外観などの結果をもとに総合評価したもので、収縮包装用フィルムとして好適なものを（○）、不適当なものを（×）とした。

実施例1～4、比較例1～2

口径50mmのインフレーション押出成形機を用いて、第1表に示す如き結晶融解熱の種々異なる熱可塑性ポリウレタン樹脂を180乃至200℃の温度で溶融混練し、インフレダイスから押出した後、引続きブローアップ比2.8乃至3.0、引取速度10乃至12m/minの条件でインフレーション成形することによって、フィルム厚さ30μの熱収縮性ポリウレタンフィルムを作成した。

これらポリウレタンフィルムについて、熱収縮

率、永久伸び、突刺強度、衝撃強度及び収縮包装後の外観等を評価した結果を第１表に示した。同表より、結晶融解熱、熱収縮率、永久伸びが共に本発明の範囲にあるものは、突刺、衝撃等の機械的強度が強く、収縮包装後の外観も良好であるなど、熱収縮性フィルムとして好適で、更にこれらの性質は参考例として示した市販のポリ塩化ビニル製熱収縮フィルム（参考例１）、及びポリプロピレン製熱収縮フィルム（参考例２）に比べて、はるかに優れたものであることが確認された。

第１表　（長さ方向／幅方向）

	結晶融解熱 (cal/g)	熱収縮率 (%)	永久伸び (%)	突刺強度 (g)	衝撃強度 (kg-cm)	収縮包装後の外観	総合評価
実施例１	0.3	35/34	11/10	1250	15	○	○
〃 ２	0.8	31/30	12/11	1200	15	○	○
〃 ３	1.5	28/25	13/13	1100	14	○	○
〃 ４	2.5	23/24	18/17	1000	12	○	○
比較例１	0	37/35	11/11	1200	14	×	×
〃 ２	3.2	15/18	22/22	800	10	×	×
参考例１	—	18/15	85/80	300	8	×	×
〃 ２	—	35/32	80/80	400	7	○	×

（注）参考例１，２のポリ塩化ビニル製及びポリプロピレン製熱収縮フィルムは、いずれも厚さ３０μのものを使用した。

実施例５～７、比較例３～４

結晶融解熱0.8cal/gの熱可塑性ポリウレタン樹脂を、口径４０mmのインフレーション押出成形機により樹脂温度 180℃にて押出した後、ブローアップ比 1.8乃至4.0、引取速度６乃至２０m/minの条件でそれぞれインフレーション成形することによって、長さ及び幅方向の熱収縮率が種々異なる、厚さ３０μのポリウレタンフィルムを作成した。

これらのポリウレタンフィルムについて、永久伸び、突刺強度、衝撃強度及び収縮包装後の外観等を評価した結果を第２表に示したが、同表より熱収縮率と永久伸びが共に本発明の範囲にあるものは突刺、衝撃等の機械的強度が強く、しかも収縮包装後の外観も良好であることが確認された。

第２表　（長さ方向／幅方向）

	熱収縮率 (%)	永久伸び (%)	突刺強度 (g)	衝撃強度 (kg-cm)	収縮包装後の外観	総合評価
実施例５	27/28	11/12	1200	15	○	○
〃 ６	40/40	18/18	1100	14	○	○
〃 ７	58/55	28/25	1000	12	○	○
比較例３	15/15	10/ 9	1250	15	×	×
〃 ４	64/62	35/34	700	8	○	×

実施例８～１０、比較例５～６

結晶融解熱1.5cal/gの熱可塑性ポリウレタン樹脂を、口径５０mmのＴダイ押出成形機を用いて、樹脂温度 190℃の条件で押出成形した。その際、ダイスから押出された溶融シートを周速３乃至１２m/minで回転する冷却ロールで引取ることにより、長さ方向の熱収縮率が種々異なるポリウレタンフィルムを作成した。

これらポリウレタンフィルムについて、永久伸び、突刺強度、衝撃強度及び収縮包装後の外観等を評価した結果、第３表に示す如く、熱収縮率と永久伸びが本発明の範囲にあるものは、突刺、衝撃等の強度が強く、収縮包装後の外観も良好であることが確認された。

第３表

（長さ方向／幅方向）

	熱収縮率(%)	永久伸び(%)	突刺強度(g)	衝撃強度(kg·cm)	収縮包装後の外観	総合評価
実施例８	27/8	17/8	1200	14	○	○
〃 ９	40/1	20/5	1100	13	○	○
〃 １０	54/1	25/4	1000	11	○	○
比較例５	17/3	14/6	1200	14	×	×
〃 ６	68/0	31/3	800	8	○	×

［発明の効果］

以上の如く本発明の熱収縮ポリウレタンフィルムは、これまでこの種のフィルムでは持ち合わせることができなかった、優れた突刺、衝撃等の機械的強度を有するほか、更にポリウレタン樹脂特有の高度な引張特性と耐摩耗性、透湿性、柔軟性並びに熱接着性等を兼備するため、収縮用包材への応用はもちろん、収縮テープ、精密作業用手袋等の産業用資材にも使用できるなど、その応用範囲は多岐にわたるものである。

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(54)[TITLE] A heat-shrink polyurethane film

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[1. TITLE]
Heat-shrink polyurethane film

[2. Claim]
It is the film which consists of a thermoplastic polyurethane resin of crystal heat of fusion 0.1 or 3.0 cal/g, comprised such that the thermal contraction rate in the 120 degrees-Celsius glycerol bath of this film is 20 % or more in at least one of the length and width directions and permanent set is 30 % or less.
The heat-shrink polyurethane film characterized by the above-mentioned.

[3. DETAILED DESCRIPTION OF INVENTION]

[INDUSTRIAL APPLICATION]
This invention relates to the heat-shrink polyurethane film which was excellent in mechanical strengths, such as a puncture, an impact, etc. very suitable as a wrapping material for contraction of various goods.

[PRIOR ART]

Conventionally, as a film for shrink packaging, heat-shrink films, such as PVC -based, polypropylene -based, and polyethylene -based, are known, It utilizes widely in the field which used each characteristics. However, a PVC -based heat-shrink film is excellent at low temperature contractile among these.

However, when it is an opposite side heat sealing, chlorine gas produces, or it adds to a sanitary problem by transfer of a plasticizer etc., it has many faults of being scarce, in mechanical strengths, such as a tension, a tear, a puncture, and an impact.

Moreover, on the other hand, as for polypropylene -based and a polyethylene -based heat-shrink film, cost is used widely at a low price.

However, on where contraction temperature is comparatively high, in this case there is a problem that the strength of a puncture, impact etc. is weak and it cracks easily, as for the film for shrink packaging of these existing, even if any are taken, at the point of the resistance with respect to a puncture and impact etc., the present condition is that what can meet the request of a user is not found.

[PROBLEM ADDRESSED]

This invention was made in view of this situation.

The place made into the objective is flexible, and its strength, such as a tension and a tear, is strong, and it is in the point of providing the heat-shrink polyurethane film which has the resistance which was moreover excellent especially to external force, such as a puncture and an impact.

[SOLUTION OF THE INVENTION]

In order that these inventors may attain said objective, a mechanical strength is strong and pays its attention to the thermoplastic polyurethane resin which has character which was moreover excellent about a flexibility and springiness.

Earnestly examination was carried out about the heat-shrink film of this polyurethane-resin base.

Consequently, if it is the polyurethane film which has a specific crystallinity and a specific heat-shrink, and permanent set, it will find out that the film suitable as a wrapping material for contraction which has mechanical strengths which were not seen, and which were excellent, such as a puncture and an impact, for heat-shrink films, such as old polychlorinated vinyl-type resin, is obtained, this invention was completed.

That is, this invention is a film which consists of crystal heat of fusion 0.1 or a thermal plastic polyurethane resin of 3.0 cal/g, comprised such that the thermal contraction

rate in the 120 degrees-Celsius glycerol bath of this film is 20 % or more in at least one of the length and cross directions.
And permanent set is 30 % or less.
It concerns on the heat-shrink polyurethane film characterized by the above-mentioned.
Hereafter, the heat-shrink polyurethane film of this invention is demonstrated in detail.
What has a thermoplasticity among the rubber-like-elasticity giant-molecule which contains a urethane group in the molecular structure which uses a bifunctional polyol, a diisocyanate, and glycol as the main raw material is named a thermoplastic polyurethane resin generically in this invention, it is a thing consisting of 1 type, or 2 or more types of thermoplastic polyurethane resins, such as adipate ester -based which the kind of raw materials, such as said polyol which it uses specifically, distinguishes, polyether -based, caprolactone ester -based, and poly carbonate-ester -based, comprised such that and the crystal heat of fusion is 0.1 or 3.0 cal/g, preferably it is 0.5 or 2.0 cal/g.

Here, when the crystal heat of fusion of a thermoplastic polyurethane resin was less than 0.1 cal/g, the tackiness was strong, and since it was easy to contact the goods and the film which involve, it became insufficient contracting the contacted part.
Or,
a cramping phenomenon is produced and a poor outward appearance is presented, as opposed to a problem critical as a wrapping material for contraction producing, if crystal heat of fusion becomes bigger from 3.0 cal/g, flexibility, springiness.
Furthermore, heat-shrink etc. falls, a heat-shrink film which is made into objective of the invention is not obtained.
In addition, the thermoplastic polyurethane resin which uses by this invention, if crystal heat of fusion is what satisfies said conditions, and also it can blend and use the thermoplastic polyurethane resin which has a crystallinity, and a normal thermoplastic polyurethane resin without a crystallinity, they are PVC -based, polyester -based, and polyamide -based within limits which do not change the character a lot, thermoplastic resins, such as an acrylic type and a polyolefin type, are blended, or even if it adds suitably a ultraviolet absorber, antioxidant, a coloring agent, a lubricating agent, etc. as required in order to improve a weather resistance, handleability, etc., it does not interfere.
For the heat-shrink polyurethane film of this invention, the thermal contraction rate in the 120 degrees-Celsius glycerol bath of this film is 20 % or more to in at least one of length and width direction again, preferably it is 30 % or more, comprised such that and permanent set must be 30 % or less, preferably 20 % or less.

This is because these inventors note the point that the tightening property in which the comparatively low coefficient of contraction was also excellent is obtained, when the thermoplastic-polyurethane film which has unique character is used for a flexibility and springiness as a wrapping material for contraction, the resistance with respect to tightening property after the coefficient of contraction of this film and packaging and puncture, and impact etc. was examined in detail.
Consequently, if the coefficient of contraction of a film becomes bigger, tightening property will improve.
However, opposite side molecular orientation progresses too much, and permanent set increases, a decrease is seen in the phenomenon in which mechanical strengths, such as a puncture and an impact, it is because it comes to be able to perform the application to the wrapping material for contraction of a polyurethane film only after both thermal contraction rate and permanent set satisfy specific conditions.
Therefore, in the polyurethane film of this invention, when thermal contraction rate in a 120 degrees-Celsius glycerol bath is 20 % or less in at least one of length and width direction, while contracting becomes insufficient and the completed outward appearance after packaging worsens, if permanent set of a film becomes bigger from 30 %, mechanical strengths, such as a puncture and an impact, will fall sharply, the inconvenient problem that the property of a polyurethane film is lost arises.

Still in this invention, when the reason for having expressed the thermal contraction rate of a polyurethane film as a value in a glycerol bath is a shrink packaging, compared with heat mediums, such as a normal hot air or steam used well, its heat conduction to a film is uniform, and it is because thermal contraction rate can be quantitatively evaluated correctly.
Moreover, the thickness of the heat-shrink polyurethane film of this invention is not suitably chosen according to the application, and it is not necessary in particular to limit it.
However, film strength, tightening property, economical efficiency.
When a feeling of a fit to the goods which it furthermore involves etc. is considered, 10 or 300 micron(s) is usually suitable for the film thickness.

[Example]
Hereafter, an Example demonstrates the heat-shrink polyurethane film of this invention in more detail.
In addition, the measuring method and the evaluation method of a physical property which were performed in this invention come out as follows.
(1) Crystal heat of fusion

A 15 mg sample is paid to a differential scanning calorimeter (DSC), this is temperature raised by the temperature increase rate of 15 degrees-Celsius/min, the heat energy released was calculated from the area of the heat generation peak which appears at the time of fusion, and it calculated for this as per 1g of samples.

(2) Thermal contraction rate
a sample film is immersed for 10 seconds during a 120 degrees-Celsius glycerol bath, and it found for thermal contraction rate in the meantime.
(3) Permanent set
The length to which the elongation between marked lines amounts to 100% is made to contract the sample film pierced to dumbbell No. 1 type after maintaining for 10 minutes, a traction and.
Permanent set was measured by following Formula.
Permanent-set (%)

$$\frac{L_1 - L_0}{L_0} \times 100$$

L0: Marked line question distance
L1: Distance between marked lines after making it contract
(4) Puncture strength
After being able to reverse a sample film and fixing cross-sectional the cylindrical ring of a diameter 75 (phi), the cone head of 53 point angles is thrust into the center of this circular film surface at the velocity of 200 mm/min, the maximum load (unit: g) until a hole opens on a film was made into puncture strength.

(5) Impact resistance
The impact resistance (unit: kg-cm) was measured on condition that full-scale 30 kg-cm and an impact head 1/2 inch using the pendulum type impact testing machine (Toyo Seiki factory film impact tester).
(6) The outward appearance after a shrink packaging, degree of about 140 - 160 of tunnel inside temperature degree-Celsius, the contraction tunnel apparatus set as passage time about 10 seconds is used, when a sample film is contractile biaxial (Example 1-7, Comparative Example 1-4)
three-ways sealing packaging, moreover, when a sample film is contractile unaxial (Example 8-10, Comparative Example 5-6)
the shrink packaging of the spray container was carried out by sleep sealing packaging, respectively.

A visual-observation evaluates the state after packaging, it is (CIRCLE) about what has favorable tightening property and a favorable outward appearance, whether contraction irregularity of which tightening property is bad or remarkable was accepted is made into (*).

(7) Comprehensive evaluation

After puncture strength, an impact resistance, and a shrink packaging, it is a comprehensive evaluation thing based on results, such as an outward appearance, the thing suitable as a film for shrink packaging was made to (CIRCLE), and the unsuitable thing was made into (*).

[Example 1-4, Comparative Example 1-2]

The thermoplastic polyurethane resin with which crystal heat of fusion as shown in Table 1 differs variously is melt-kneaded at the temperature of 160 or 200 degrees-Celsius using the inflation extrusion machine of 50 mm of aperture diameters, after extruding from an inflation dice, the heat-shrink polyurethane film of film thickness 30 micron was created by carrying out inflation molding succeedingly on condition that a blow up ratio 2.8 or 3.0, the taking over velocity 10, or 12 mmin(s).

About these polyurethanes film, the result which evaluated the outward appearance after thermal contraction rate, permanent set, puncture strength, an impact resistance, and a shrink packaging etc. was shown in Table 1.

Both the things in the range of this invention have crystal heat of fusion, thermal contraction rate, and permanent set mechanical strengths stronger than a same table, such as a puncture and an impact, the outward appearance after a shrink packaging is also favorable, etc. suitable as a heat-shrink film, furthermore, these characteristics are compared with the commercial heat-shrink film made from a PVC (Reference Example 1) shown as Reference Example, and the heat-shrink film made from a polypropylene (Reference Example 2), it was checked that it is excellent.

表 1 (長さ方向/巾方向)

実施例1	0.3	55/54	12/10	1250	13	○	○
〃 2	0.6	51/55	13/11	1280	15	○	○
〃 3	1.0	56/75	13/13	1160	24	○	○
〃 4	1.3	52/74	16/17	1050	12	○	○
比較例1	0	37/35	11/11	1260	14	×	×
〃 2	3.1	45/56	22/21	860	10	×	×
参考例1	—	60/61	85/84	310	6	○	×
〃 2	—	95/91	66/66	490	7	○	×

Table 1 (length direction / width direction)

Row (left to right): Crystal heat of fusion, thermal contraction rate, permanent, puncture strength, impact resistance, outward appearance of contraction package packaging, joint evaluation

Column (top to bottom): Example 1, Example 2, Example 3, Example 4, Comparative Example 1, Comparative Example 2, Reference Example 1, Reference Example 2

Notes
Each of products made from a PVC of Reference Example 1 and 2 and heat-shrink films made from a polypropylene used the thing of the thickness 30 micrometer.
(Note) Each of products made from a PVC of Reference Example 1.2 and heat-shrink films made from a polypropylene used thickness 30 micron.

[Example 5-7, Comparative Example 3-4]
After extruding the thermoplastic polyurethane resin of crystal heat-of-fusion 0.8 cal/g at resin-temperature 180 degrees-Celsius by the inflation extrusion machine of 40 mm of aperture diameters, the thermal contraction rate of length and width direction created the polyurethane film of variously different thickness 30 micron by carrying out inflation molding on condition that a blow up ratio 1.8 or 4.0, the taking over velocity 6, or 20 mmin(s), respectively.
About these polyurethane films, the result which evaluated the outward appearance after permanent set, puncture strength, an impact resistance, and a shrink packaging etc. was shown to table 2.
However, from the same table, both the things in the range of this invention had thermal contraction rate and permanent set strong mechanical strengths, such as a puncture and an impact, and, moreover, it was checked that the outward appearance after a shrink packaging is also favorable.

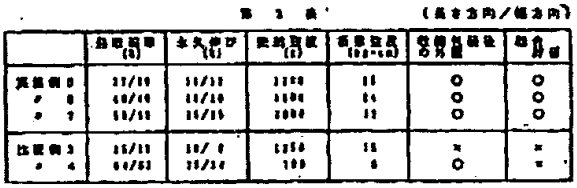

Table 2 (length direction / width direction)

Row (left to right): thermal contraction rate, permanent set, puncture strength, impact resistance, outward appearance of contraction package packaging, joint evaluation

Column (top to bottom): Example 5, Example 6, Example 7,
Comparative Example 3, Comparative Example 4

[Example 8-10, Comparative Example 5-6]

Extrusion molding of the thermoplastic polyurethane resin of crystal heat-of-fusion 1.5 cal/g was carried out on condition that resin-temperature 190 degrees-Celsius using the T-die extrusion machine of 50 mm of aperture diameters.

The thermal contraction rate of the length direction created a variously different polyurethane film by taking over with the cooling roll which rotates the melting sheet which it extruded from the dice by the convergence 3 or 12 mmin(s) at that time.

About these polyurethanes film, the outward appearance after permanent set, puncture strength, an impact resistance, and a shrink packaging etc. was evaluated.

Consequently, it was checked as shown in Table 3 that the thing in the range of this invention has strong strength, such as a puncture and an impact, and the outward appearance after a shrink packaging also has favorable thermal contraction rate and permanent set.

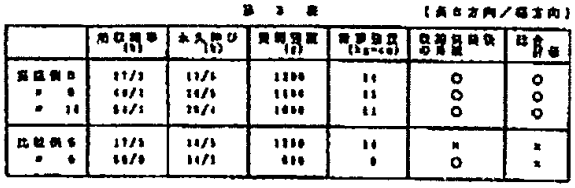

Table 3 (length direction / width direction)

Row (left to right): thermal contraction rate, permanent set, puncture strength, impact resistance, outward appearance of contraction package packaging, joint evaluation

Column (top to bottom): Example 8, Example 9, Example 10,
Comparative Example 5, Comparative Example 6

[EFFECT OF THE INVENTION]

And also the heat-shrink polyurethane film of this invention has mechanical strengths which it was not able to have with this kind of film until now and which were excellent, such as a puncture and an impact, as mentioned above.

Since it has an high degree tension property and an high degree antiwear quality further peculiar to a polyurethane resin, a moisture permeability, a flexibility, heat

boundable, etc., for the application to wrapping material for contraction, of course, it can use also for industrial materials, such as a contraction tape and a glove for precision operation, and the application range is various.

[REPRESENTATIVES] Kazumi Ogawa